DECLASSIFIED
DATE
AUTHORIZED BY

SCUMMING OF GYPSUM-BEARING QUEENSTON SHALE

K.E. Bell
Mineral Processing Laboratory

January 1987

Project: 3.0.2.9.99
Cost Recovery in Minerals Processing

Job No. 025235

MICROMEDIA

15 pp

MINERAL SCIENCES LABORATORIES
DIVISION REPORT MSL 87-2 (CR)

CONFIDENTIAL

CONFIDENTIAL

SCUMMING OF GYPSUM-BEARING QUEENSTON SHALE

by

K.E. Bell*

SUMMARY

Queenston shale in the lower strata of the deposit used for brickmaking by Canada Brick Co., Burlington, Ontario, is contaminated with nodules assumed to be gypsum. This was verified by XRD analysis, which detected only gypsum and some occluded shale. Solubles extracted from the ground shale were identified as gypsum, calcite, bassanite and a trace of halite, comprising a total of 0.265 wt %. The white scum from plant- and laboratory-dried bricks was found to comprise only gypsum.

Tests in-liquidus indicated that additions of at least 0.7 wt % of $BaCO_3$ were required to essentially immobilize the sulphates. Above a minimum addition of 0.3 wt % $BaCO_3$, a progressive reduction in sulphates in solution was observed. Hence, further in-liquidus tests were conducted using a combined basic addition of $BaCO_3$ plus other additive materials indicated in the literature to be of possible value for inhibiting sulphate scumming: bentonite, carboxymethyl cellulose (CMC), calcium lignosulphonate (Lignosol), sodium silicate, boric acid and sodium tetrapyrophosphate. Lignosol and boric acid were judged most effective, followed by CMC.

Test briquettes were extruded with additions of $BaCO_3$ alone, and combined with other materials selected from the above. Because a uniform white scum was difficult to perceive on the dried briquettes, several were fired to a temperature normal to production, rendering the scum visible against the reddish fired material. No scum was apparent on briquettes containing o.75% $BaCO_3$, $BaCO_3$/Lignosol and $BaCO_3$/CMC.

On the basis of criteria including extrusion and drying behaviour, scumming and estimated cost, $BaCO_3$/Lignosol was judged the most appropriate additive, followed by $BaCO_3$/CMC.

---

* Research Scientist (retired), Ceramics Section, Mineral Sciences Laboratories, CANMET, Energy, Mines and Resources Canada.

INTRODUCTION

Canada Brick Company Limited, Streetsville, Ontario, requested assistance from CANMET in seeking a solution to a problem of discolouring white scum that appears on burned clay brick manufactured from a Queenston shale deposit in Burlington Ontario. The source of the scum is assumed to be gypsum, which occurs in nodules in the lower strata of the deposit. This material is reported not to be amenable to prevention of scumming by treatment with economically acceptable amounts of barium carbonate, the usual preventative. Currently, the material is utilized by applying a white engobe to the exposed surfaces of the bricks, thus negating the visual effects of the scum: for obvious economical reasons it is desireable to be able to use the full depth of the deposit for manufacture of clear brick-red products.

In discussion with technical plant personnel, it was agreed that CANMET should analyse the impurities (gypsum modules) and the resultant scum, and search the relevant literature on solubilities and potential sequestering agents that might inhibit scumming alternative to or in concert with barium carbonate. Based on these results a series of wet chemical tests would be employed to evaluate the inhibiting effects of selected promising materials: it was agreed that minimal emphasis would be applied to soluble salts such as alkalies that are themselves known to be scumming agents. The effect of up to six of the more promising materials would then be evaluated for scumming in extruded briquettes.

The work was performed under Project 3.0.2.9.99, Cost Recovery-Ceramics, Job No. 025235.

MATERIALS

The company provided the following materials for examination:

1) Gypsum Nodules: Three irregular shaped nodules, ranging from about 7 to 15 mm equivalent diameter, were reported to be from 3 widely separated locations in the shale pit. They were white, with inclusions of red and grey-green shale. Representative aliquots, excluding shale

contaminated zones, were selected for analysis by powder X-ray diffraction using a Guinier-deWolff four-sample camera; a sample of chemically pure gypsum was employed as an internal comparitive standard. All three samples are identical; the overwhelmingly dominant constituent is gypsum. A search of the diffraction index revealed no identifiable trace of salts of sodium, potassium or magnesium, nor any carbonates or chlorides. One line in the X-ray diffraction pattern remains unidentified: a very very weak (vvw) line at 2.96 Angstroms may indicate a trace of celestite (strontium sulphate) but other identifying lines are absent or masked by the strong pattern for gypsum.

2) Shale: Ground red Queenston shale, reported to be from the lower strata of the pit. Occasional particles of gypsum were discernable. The shale, as received, contained 6.4% moisture, based on dry weight.

An attempt was made to quantitatively determine the solubles content of the shale. A representative aliquot of 200 g (dry weight equivalent) of shale was selected by riffling. The sample was submitted to two cycles of dissolution, each in 2000 mL of distilled water at room temperature for 48 h. After each cycle, the supernatant liquid was decanted into a suction filter flask through a Buchner funnel, employing two sheets of dense Whatman paper to prevent visible passage of fine clay particles. Following the second cycle, the sample was transferred to the filter funnel and washed repeatedly (six times) with 200 mL aliquots of distilled water until the filtrate revealed no sulphates with the standard silver nitrate test. The filtrate was evaporated to dryness on a steam bath. The residue was collected and final dried below 85°C (to prevent dehydration of the gypsum), weighed, and the solubles calculated to be 0.265 % of dry weight of shale.

The sample of solubles was analysed by X-ray diffraction using the Guinier camera. The constituents of the samples, in decreasing order of abundance, were identified as gypsum ($CaSO_4 \cdot 2H_2O$ - assumed to be primarily from the nodules), calcite ($CaCO_3$ - from the high-lime shale), bassanite (dehydrated gypsum - probably a result of over-drying the sample, but possibly disseminated in the shale and the source of material ultimately forming the nodules), plus a trace of halite

(NaCl-from the shale, as none was detected in the nodules). Hence, gypsum and related sulphate comprised probably two-thirds to three-quarters of the sample.

3) Wet and Dry Bricks: Samples were suppled of bricks manufactured from the lower strata of shale containing the nodules: two freshly extruded bricks, wrapped in plastic to prevent drying, and two bricks dryed in the plant dryers. It was indicated that the bricks contained additions of both bentonite and lignosulphonate to improve extrusion behaviour of the shale. The bricks were coated with a white engobe and sand on the face and both ends.

Some white scum was perceptible on the sides of the plant-dried bricks, uniformly distributed. It was more apparent on the backs of the bricks, with some concentration where the bricks had been cross-set.

An attempt was made to concentrate the solubles on drying the wet bricks. Each was tightly wrapped in polyethylene and an opening measuring 2.5 x 5.0 mm was made centrally on the back of each brick to provide a restricted drying area. One brick was dried rapidly in a laboratory oven, one slowly, first at room temperature, then in the laboratory oven. The attempt was only partly successful as the wrapping loosened, probably owing to shrinkage of the drying bricks and stretching of the heated plastic foil. Under these conditions no difference due to rate of drying could be observed. There was no apparent concentration of white salts over the exposed area, but a rim of brownish scum was evident around the holes in the foil. The colour was presumably due to lignosulphonate, possibly containing other soluble salts.

The side and back surfaces of both plant-dried and laboratory-dried bricks were scraped to remove the concentrated salts. All scrapings were combined into a single sample. The soluble salts were redissolved in a large excess at distilled water, the contaminating clay constituents were removed by filtering and the filtrate dried as before. Gypsum alone was identified by X-ray diffraction analysis of the concentrated salts. Hence, it is concluded that the scum is derived solely from the nodules.

LITERATURE

Ceramic Abstracts were deemed the most appropriate source of relevant information. The indexes dating back to 1971 were searched under all headings considered to be directly or peripherally relevant, revealing only 10 citations of possible interest. For literature of 1970 and prior, the search was conducted through the writer's card file, 129 entries, prepared during a comprehensive literature search undertaken for a previous investigation. Solubility data for most of the relevant salts are available (1). Consultation with CANMET chemists, particularly those involved in SO_2 abatement, revealed no familiarity with the problem of scum, nor any useful suggestions.

A preponderance of the citations could be eliminated from consideration as they dealt with efflorescence on fired brick without reference to scum as a precursor. Others dealt with dryer scum arising from sulphates carried over with waste heat, rather than those contained in the raw material per se. Not surprisingly, most of those of direct relevance dealt with elimination of scum by barium carbonate additions. By 1946, this was a common practice in Canadian brick plants (2), and is currently almost universally employed. The problem of scumming has been studied in depth and reported by Brownell (3). Many problems of scum control arise from variation in sulphate content in the material, either through local concentration in the deposit or through changing moisture content in the material. It must be borne in mind that the calcium sulphates responsible for scumming here are at best sparingly soluble: the solubilites quoted are equilibrium values, achieved over a considerable time and/or in substantial amounts of water, neither of which conditions are particularly applicable to brickmaking processes. Similarly, barium carbonate is of low solubility (which lowers its toxicity to a level acceptable for in-plant use), and its effective solubility in processing varies with its crystallinity and particle size (4). Thus, determination of the optimum addition of barium carbonate is determined empirically by, e.g., the Baridex method (5) as opposed to theoretical consideration of the chemical reactions involved, although the latter are well known and often reported, e.g. Ref. 6. Given the composition of the offending soluble salts in this case, barium

additions should be effective: the quantity required and the attendant cost is reportedly prohibitive.

Successful alternative or complimentary treatments are rare in the literature. Highly anion-adsorptive clays such as bentonite might be expected to inhibit sulphate ion mobility by retention in the charged double-layer responsible for the gel structure: however, the bonding would be weak in low water contents. Lignosulphonates reportedly prevent sulphate scumming; Kimberly-Clark's "Additive A" (possibly a Ba-exchanged lignosulphonate) is claimed to be effective. A sulphate scum arising from fly-ash additions, reportedly not amenable to $BaCO_3$, was prevented by lignosulphonate addition (7). However, in the wet Burlington bricks dried in this laboratory (above), lignosulphonates were observed in concentration at the surfaces, presumably accompanied by sulphates. Similarly, Phelps (8) has reported the neutralization of sulphates in sanitaryware bodies by huminates derived from alkali (NaOH) treatment of the lignitic material in dark ball clays. At the higher pH's, the huminates form a colloidal gel that presumably sequesters sulphates: the effect on scumming, if any, is not reported. Sodium silicate, which forms a more marked gel than lignosols, is widely used as a deflocculant in white wares, thus might sequester sulphate ions. The silicate itself does migrate with the water during slipcasting, to which the deterioration of plaster moulds is often attributed. The deflocculating effect of sodium silicate has, however, been blamed by Laird (9) for increased scumming of bricks owing to a reduction in rate of drying, which allows more time for dissolution of sulphates. Sarker and Greminger (10) report the use of methylcellulose polymers as processing aids: in addition to imparting lubricity and strong binding, they note that "(they), by thermal gelation, inhibit binder migration during drying", thus could be expected to restrain migration of salts trapped in the gel structure. Currently a wide variety of polymers are available, opening the door to extensive investigation, which will reportedly be undertaken by Canada Brick Limited.

Tricalcium aluminate is reported by Goodwin and Clews (11) to react with soluble sulphates to form insoluble Ca-S-aluminate. The addition of Portland cement clinker high in $3CaO\text{-}Al_2O_3$ is recommended as a solution to sulphate efflorescence: it seems probable that the time required to

dissociate the material and react is beyond that available during extrusion and drying of bricks. Additions of sodium meta-,pyro-, or poly-phosphate, according to Andrieth (12), prevent formation of "white bloom" on bricks and improve and darken the red colour; although he relates the mechanism to formation of insoluble calcium compounds, it seems likely that the deflocculating effect of the sodium phosphates (to produce a denser body at lower water content) is a primary factor. There remains, too, the possibility of undesireable phosphate emissions during firing. In a similar vein, Kirsch and Nadler (13) have most recently reported on the efficacy of a variety of laboratory-prepared barium compounds: the most successful additives were barium phosphates and borates. Solubility data are not given, but it seems likely that higher solubilities vs. that of barium carbonate, would be primarily responsible for increased sulphate immobilization, similar to that well-known for the more soluble barium chloride, hydroxide and bi-carbonate. The latter are not used industrially owing to their high toxicity. Minor phosphate and borate additions to barium carbonate were considered of possible interest, although major additions of phosphates would likely give rise to undesireable kiln emissions, of boron to borate scum and efflorescence (14).

PROCEDURE AND RESULTS

The efficacy of barium carbonate additions alone was examined in liquidus. One hundred grams (equivalent dry weight) of shale was placed in each of a series of graduated beakers and each was filled to the 500 mL mark with distilled water. Barium carbonate (Analar, precipitated fine 99.5% chem. pure) was added to successive beakers in amounts of 0.0, 0.1, 0.2, 0.3, 0.5 and 0.7% of dry weight of clay, thoroughly stirred mechanically and allowed to settle overnight. Aliquots of 10 mL of supernatant liquid from each beaker were transferred to test tubes, to each of which was added an excess of barium chloride in the standard test for sulphate. The intensity of the precipitate formed was judged by eye.

The material with no barium carbonate addition produced a moderately heavy white precipitate, which was not perceptibly reduced by additions of 0.1 and 0.2% $BaCO_3$. A slight reduction in the intensity of the precipitate

was observed for the 0.3% addition, which became significant with 0.5% $BaCO_3$. With addition of 0.7% only a slight precipitate was formed. Hence, it was concluded that a threshold value of at least 0.25% (of this type of $BaCO_3$) would be required in conjunction with minor accessory additions to successfully inhibit scumming.

The tests in liquidus as described above were repeated with a series of selected accessory additives, with a basic addition of 0.25% $BaCO_3$, with the following results:

	Accessory Additive	Precipitate
1)	0.20% Lignosol BD	light to very light
2)	1.5% Wyoben bentonite	moderate to strong
3)	0.15% carboxymethylcellulose (CMC) (viscosity: 3000 cps)	light (in some suspended clay material)
4)	0.20% sodium silicate	evident but indeterminate amount, owing to high volume of suspended clay even after 72 h settling
5)	0.15% boric acid	very slight (strongly flocculated)
6)	0.20% sodium tetrapyrophosphate ($Na_4P_2O_7 \cdot 10H_2O$)	heavy - more than shale with no additive

Notes: with lignosol the supernatant liquid was discoloured but not gelled; with bentonite a trace of suspended material remained but did not impair evaluation of the amount of precipitate, also with CMC (probably due to a weak gel); strong deflocculation by sodium silicate inhibited settling (although a strong precipitate formed, its true extent could not be evaluated); with phosphate, BaCl formed a strong precipite in a gel (lowered pH?), which unfortunately broke down permanently with slight agitation.

The most promising accessory additives appeared to be lignosol and boric acid, followed by CMC.

The scum inhibition of selected additives was evaluated on laboratory-extruded bricks, made from the raw shale supplied: sufficient material was available for 5 sets of 6-7 briquettes each. As most additives were expected to influence extrusion behaviour, details were observed and recorded:

No.	Additive	Extrusion
1.A	shale, as received 13.6% water (% of dry weight of shale	purposely soft to enhance scum; pressure for extrusion 3-4 tonnes
2.	0.75% $BaCO_3$ 12.5% H_2O	good, stiff column, ≈ 6 tonnes
3.	0.25% $BaCO_3$ 0.20% Lignosol BD 12.5% H_2O	good, stiff column, ≈ 5 tonnes
4.	0.25% $BaCO_3$ 0.15% CMC 13.5% H_2O	very stiff column, ≈ 9-10 tonnes (reflects water absorbed in gel)
5.	0.25% $BaCO_3$ 0.15% boric acid 13.0% H_2O	good, very stiff column, ≈ 7 tonnes

The extruded briquettes were marked for identification and placed on expanded metal trays for drying. Half were initially dried rapidly in a laboratory oven at 85°C, half were first air-dried at ambient temperature for 24 h. All were final dried at 105°C. The presence of any light scum was difficult to perceive, owing to the natural greyish red colour of the dry briquettes. Nevertheless, the as-received material was judged to bear a thin white scum on the slow dried specimens and possibly on the fast dried specimens; both showed brownish markings on the bottoms where drying was inhibited by the solid sections of the metal (enamelled) tray. Test No. 2 (0.75% $BaCO_3$) was judged to be free of whitish scum, with minor brownish marks at contact with the setter. Test No. 3 (Lignosol) showed an overall brownish scum when dried rapidly, with concentrations at the sharp edges and corners; when slow dried the brown scum was concentrated in a speckled

fashion apparently related to coarse (porous ?) shale particles immediately below the surface. Test No. 4 (CMC) was judged essentially clear of scum on both fast and slow drying. Test No. 5 (Boric Acid) showed brown speckles on the three exposed sides with some concentrations on the bottom opposite the holes in the setter: on slow drying brown scum was also concentrated on the sharp edges at the top of the briquettes.

The difficulty in identifying the presence of scum on the dried briquettes was overcome by firing them, rendering the disfiguration more evident against the reddish fired colour of the briquettes. The specimens were fired in an electrically heated laboratory kiln to 1030°C (1886°F) in 22 h, and allowed to cool at the normal rate of the furnace. The following observations were recorded:

Test No. 1A (no additive): pronounced white scum on upper surfaces, sides and ends of specimens, lesser concentration on bottoms; some evidence that fast drying produced more scum, particularly evident on the bottoms of the specimens.

Test No. 2 (0.75% $BaCO_3$): no distinctive scum, although of slightly lighter fired colour than Tests 3 and 4, possibly attributable to light streaks attributed to high-lime particles dragged along the die surfaces; no discernable difference due to drying rate. (Note: lime-popping was indicated on some specimens on this firing schedule).

Test No. 3 ($BaCO_3$ + Lignosol): light red, no evidence of scum, some lighter streaks, as above; no discernable difference due to drying rate.

Test No. 4 ($BaCO_3$ + CMC): similar in all respects to Test No. 2.

Test No. 5 ($BaCO_3$ + boric acid): uneven brown scum, mostly concentrated in streaks and blotches, and the light (limey) streaks noted above are strengthened in intensity, probably due to reaction with boric acid; fast drying results in distribution of the discolouration over all surfaces of the specimen, slow-dried specimens showed scumming on the upper surface only, with concentration at corners and edges.

CONCLUSIONS

1. The gypsum nodules in the shale deposit are unquestionably responsible for the bulk of the scum. There is some indication that additional calcium sulphates (identified here as bassanite) may be disseminated throughout the shale. Other soluble salts in the shale include calcium carbonate and a trace of sodium chloride: these were not found to contribute to scumming of either plant- or laboratory-made bricks.

2. To fully neutralize the sulphate required, an economically excessive addition of at least 0.7% of $BaCO_3$ was indicated. Under actual operating conditions, the precise requirement will vary according to the solubility (particle size, crystallinity) of the $BaCO_3$ employed, the amount of water in the bricks, and the method of addition and distribution throughout the shale. The in-liquidus tests also indicated that a minimum addition of about 0.3% was required before any effective sulphate reduction was obtained. This result poses the possibility of acceptably inhibiting scum with lower additions than the optimum or with a basic $BaCO_3$ addition in combination with one or other of the materials identified in the literature survey.

3. Of the accessory scum inhibitors evaluated in this work, only carboxymethy cellulose and Lignosol were effective. Bentonite and sodium silicate did not adsorb/sequester sulphate ions effectively in solution. Boric acid flocculated the shale with adverse effects on extrusion (high power): it also produced a dirty fired scum.

   Combined additions of $BaCO_3$/Lignosol are effective, and probably most economical. Extrusion is normal, or slightly improved, and higher dry strengths are to be expected. The brown dryer scum owing to lignosulphonates burns off cleanly during firing. Trials using the type of $BaCO_3$ in use at the plant, and the available mode of mixing and addition, will be required to determine the optimum amounts and proportions.

Combined additions of $BaCO_3$/CMC are equally effective for scum inhibition. In these laboratory trials, this combination resulted in high power requirements for extrusion and some resultant cross-cracking tendencies. As a portion of the water will be tied-up in the gel structure, more water of plasticity will be required, with attendant increased energy requirements for drying. A further addition of an appropriate amount of water should resolve the extrusion problems encountered in the laboratory; in fact, the lubricity of the gel would be expected to improve extrusion. A small addition to the mixing tanks would be useful to inhibit settling of the $BaCO_3$ and assist uniform dispersion in the pugmill. It should be useful to seek alternative polymers available at lower cost. (A high priority should be given to materials forming a high-viscosity gel, which will inhibit migration of the gel and entrapped salts).

4. There is evidence that slow drying results in decreased scum, probably owing to longer time for chemical reaction with the additives. Whenever possible, ample time for such conditioning should be provided in the holding room preceding the dryer.

ACKNOWLEDGEMENT

The author is indebted to H.C. Childe, Mineral Processing Laboratory, for the X-Ray Diffraction analyses.

REFERENCES

1. Handbook of Chemistry and Physics; Pub. Chemical Rubber Co., Cleveland, Ohio.

2. L.P. Collin, "Methods of Using Barium Carbonate for the Prevention of Scum"; Clay Products News and Ceramic Record; 20; 10, 7-9; 11, 6-9; 1946.

3. W.E. Brownell, "Scum and Its Development on Structural Clay Products"; Structural Clay Products Research Foundation; Report No. 4; 1955.

4. W.E. Moody, "Effect of Particle Size and Deflocculation of Barium Carbonate on Scum Control"; Ceramic Bulletin; 44; 8, 604-607; 1965.

5. Baridex

6. A.D. Franz, "Normal and Abnormal Mechanisms of Scum Formation"; presented at the 68th Annual Meeting, The American Ceramic Society, Washington, D.C.; 1966.

7. W.H. Bauer, "Method of Making Ceramic Product and Moldable Mix"; U.S. Patent 2,833,659; 1958.

8. G.W. Phelps, "The Role of Organic Matter in Slip Casting"; Ceramic Bulletin; 38; 5, 246-250; 1959.

9. R.T. Laird, "Scum and Soluble Salt in Wealden Clays"; Br. Clayworker; Nov., 1963.

10. N. Sarkar and G.K. Greminger, Jr., "Methylcellulose Polymers as Multifunctional Processing Aids in Ceramics"; Ceramic Bulletin; 62; 11; 1280-1284, 1288; 1983.

11. J.F. Goodwin and F.H. Clews, "Tricalcium Aluminate as an Addition to Brick and Tile Bodies"; T.B.E. Colloquium on Efflorescence reported in Ziegelindustrie; 16; 18, 670-; 1963; and in British Clayworker; July, 1963.

12. L.F. Andrieth, U.S. Patent 2,880,099; March 31, 1959.

13. R. Kirsch and J.P. Nadler, "Deflocculation and Precipitation of Soluble Sulphates in Ceramic Casting Slips"; Ceramic Forum International; 6; 259-262; 1986.

14. K.E. Bell, "Investigation of Efflorescence on Facing Brick"; Mines Branch Investigation Report I.R. 63-27, Mineral Processing Division, CANMET, Energy, Mines and Resources Canada.